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A Study of the Effect of Surfaces on Oxygen Atom Recombination at Low Pressures

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ABSTRACT

The purpose of this work is to determine the catalytic effect of surfaces on constituents found in the upper regions of the atmosphere in the pressure region of 10^{-5} to 10^{-8} torr. The work is directly related to the problem of satellite experiments involving mass spectrometric measurements in this region where surfaces may alter or react with oxygen and hydrogen atoms.

This interim report discusses the experimental techniques and many of the direct and indirect problems involved and the results obtained today.

What surfaces may be used most satisfactorily at this time is still a major question. Some surfaces can be excluded others which seem to be satisfactory have to be tested further to determine if they are reliable under all conditions. The problem is especially complicated due to the presence of oxygen atoms and hydrogen atoms.

In addition there is the special problem of the high relative velocity of the atmospheric particles ($>$ 4ev for O-atoms) which impinge on the satellite at velocities corresponding essentially to the velocity of the satellite. Such highly energetic collisions may produce anomolous results, which are difficult to predict from the results of laboratory experiments.

Discussion:

The study of reaction kinetics is complicated by the number of variables present: pressure, temperature, constituents, impurities, flow paths, reaction times, etc. Low pressures studies are difficult because of the large diffusion coefficients involved and the lack of streaming. Surfaces normally covered by relatively inert adsorbed gas layers may become directly exposed and mixtures of O and H-atoms especially may react under these conditions.

At this time we have an operating system including a reaction tube maintained at less than one millimeter total pressure with capability of streaming through it either O or H-atom or both, from which side-streams of known concentration may be fed into reaction volumes operating at a few microns and down to 10^{-5} mm and even much lower. Calibrated flow controls were built and flow characteristics determined. At these low pressures it is very difficult to maintain negligible back diffusion from the pumping system and therefore liquid helium for cryogenic pumping was used to obtain the best conditions. The desired steady-state pressure results from a balance of input and output flows.

First experiments have been made in determining the ozone formation with and without sample surfaces.

To get results in a relatively short time we made our first experiment in the region of 10^{-6} mm, but obviously these can now be extended without any difficulty into regions of pressure several decades lower.

After a run of several hours under these conditions a weak blue haze could readily be observed when the liquid helium was removed. Oxygen atoms result in ozone formation at low temperature and this conversion is used to indicate the oxygen atom concentrations. The interesting kinetic details are omitted here. The evaporated gas was transferred into a cell by means of silica gel and liquid N_2 cooling, and the content of ozone could be readily measured by its light absorption. For minor amounts of ozone we may have to transfer the ozone-oxygen mixture by helium cryogenic techniques.

Mass spectrometric methods for measuring oxygen atoms in the laboratory at these low pressures do not seem feasible in general at least without very high expense and considerable effort. The mass spectrometers under flight conditions are obviously superior in performance to those in the laboratory with the pumping facility of "outer space".

One alternate possibility if needed is O-atom measurements via the resonance lines 1302, 1304 and 1306 A analogous to methods used in atomic absorption apparatus. For this case our calculations indicate O-atom concentrations might be measured in the 10^{-5} to possibly 10^{-7} torr region. Certain complications occur, however, because of the relative velocities of the system to the O-atoms for any space applications.

In addition we are, however, now developing a micro-photometric method with the goal to measure the concentrations of very rarified particles with application to problems of the upper atmosphere. In this connection we have shown in earlier work, certain two body recombinations occur with emission of light such as:

$$NO + O \rightarrow NO_2 + h\nu \qquad k_1 = 6\ 10^{-17}\ (\text{part/cc})^{-1}\text{sec}^{-1}$$

$$SO + O \rightarrow SO_2 + h\nu \qquad k_2 = \quad 10^{-15}\ \quad " \quad " \quad "$$

It can easily be seen that if O-atoms at 10^{+10} particle concentration prevail and we add through a leak sufficient amounts of NO to yield a stationary state of 10^{+10} particles of NO, then 6×10^3 light quanta cc/sec are emitted. Our arrangement should be sensitive enough to measure this light intensity readily. (At present SO would not appear feasible although the rate coefficient is larger).

Obvious it would be hard to send such an instrument on a flight without major costly technical developments. However, in the laboratory it seems to be a very valuable tool because continuous measurements within seconds could be performed and even additional experiments concerning interference of absorbed O-atoms on surfaces could be determined by this technique. This would involve the rate of equilibration of an adsorbed, O-atom layer on a surface.

At present our general conclusions involve much of the known previous results and result especially in concern for the effect of H-atoms when mixed with O-atoms. Also the very fast atmospheric particles may not "bounce" on first collision with the vehicle, but in certain cases even be imbedded in the skin. Teflon, however, does appear to hold up reasonably in a test system we have used and does not react with H-atoms significantly as was known, nor with O-atoms even at relatively high pressures. Therefore, Teflon may be appropriate for a surface which is not exposed to direct impact of the atmospheric particles. For the entrance area where particles with high relative energies will impinge, surface with rigid crystal lattice will have to be investigated.